Solution Synthesis of Columnar ZnO Film Structures

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Nucleation and Growth of Extended Film Structures

Objectives:

- Develop a generalized solution-based approach for growing oriented nanostructured films.
- Develop systematic methodology to control film structure.
- Apply to several representative systems, including oxides, polymers, self-assembled nanosilicates, metals, and non-oxides……

Approach: Control Nucleation and Growth

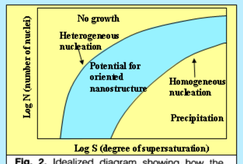


Fig. 2. Idealized diagram showing how the number of nuclei (*N*) is predicted to vary with supersaturation (*S*) and the net interfacial energy for nucleation (σ) according to classical nucleation theory. Curve 1 is representative of homogeneous nucleation behavior. Curve 2 is calculated by the assumption that all parameters are identical except σ, which is one-half of the homogeneous value. Curve 2 is indicative of net interfacial energies associated with heterogeneous nucleation.

Seeded Growth

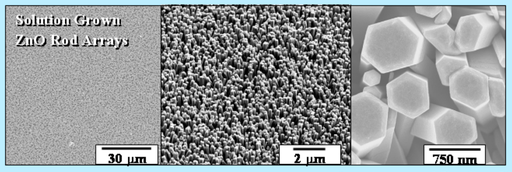
Or

Active Surface Mediated Growth

- Nucleation: start with a dilute solution and a low temperature without any precipitation in the initial stages.
- Growth: Use growth modifiers to control - apply molecular modeling to develop/understand.
- Model System: ZnO.

Baseline Process Growth of Arrays of ZnO Rods

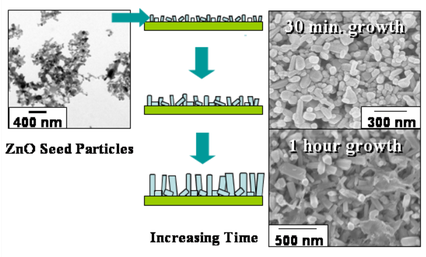
1) Use seeded nucleation: apply layer of ZnO nanoparticles to substrate.
2) Place substrate in solution containing 0.030M $Zn(NO_3)_2$ and 0.030M hexamethylenetetramine (HMT)*
3) Grow rods: react solution containing substrate at 60°C for 3 days.



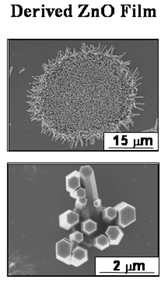
*Vayssieres et al., *J. Phys. Chem. B* 2001

Nucleation of ZnO Film Structure

Seeded Nucleation



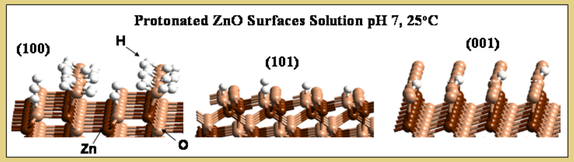
Templating Using Patterned Sol-Gel Derived ZnO Film



Modeling: "Design" of Growth Modifiers

Step 1: Create ZnO surfaces as they would exist in H_2O.

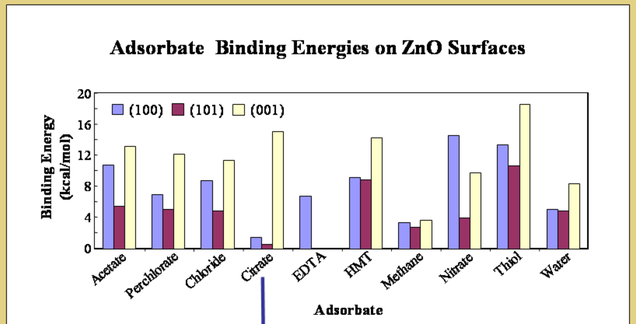
- Determine surface protonation state using a model based on bond-valence and a correlation with experimental data on the acidity of aqueous metal complexes.
- Apply the *Charge Distribution Multisite Complexation* model developed for oxide and hydroxide minerals - the CD-MUSIC model (Heimstra et al., 1996).

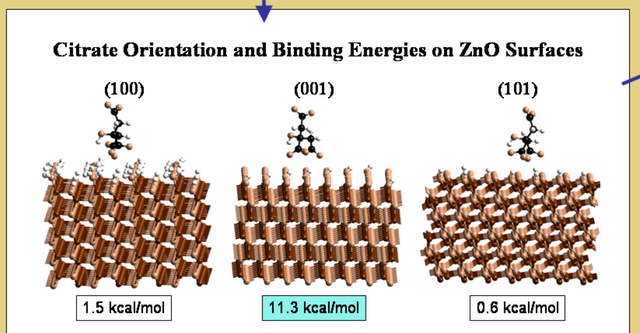


Step 2: Perform molecular mechanics simulations to calculate adsorbate binding constants.

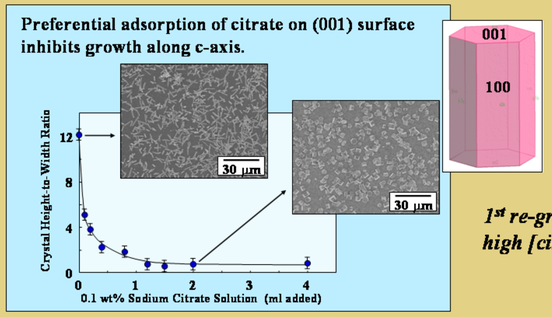
- Create 2-D periodic surfaces
  1) Charge-distribution determined on 3-D periodic slabs using UFF*
  2) Average charges for internal Zn and O atoms transferred to 2-D periodic model
  3) Average charges for each type of surface site transferred to 2-D model
- Optimize structure of ZnO surface without constraints to allow surface relaxation
- Find minimum energy configuration for adsorbate-surface interaction
- Calculate energy profile for adsorbate-surface interaction as a function of adsorbate/surface distance with fixed adsorbate/surface geometry
- Correct profile by finding minimum energy adsorbate/configuration at each point along energy profile

*(Rappé and Goddard, 1991)

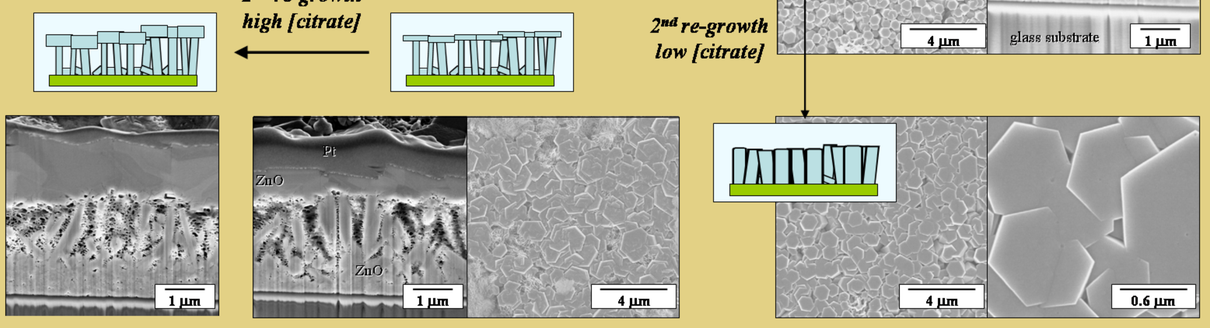




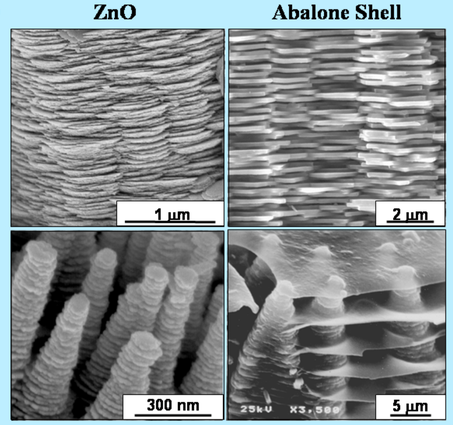
Use of Citrate as ZnO Growth Modifier



Modification of ZnO Array Structure via Re-Growth in the Presence of Citrate

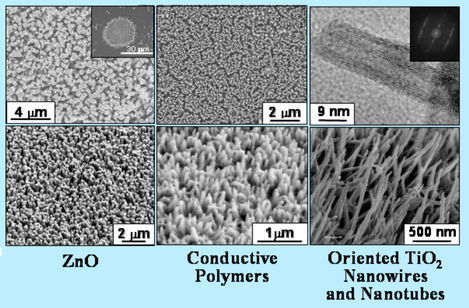


Biomimetic ZnO Nanostructures

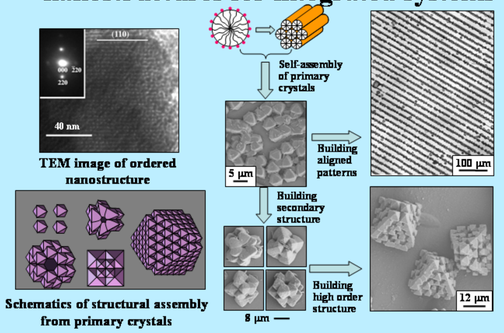


Systematic morphology control of oriented nanostructures based on fundamental understanding of the crystal surface chemistry and organic – inorganic interactions

Generalized approach for controlled nucleation and growth, patterning and alignment of oriented nanostructures



Multiscale self-assembly of oriented nanostructures for integrated systems



Potential: chemical and biosensing, energy storage and conversion, optical emission, catalysis, actuators and transducers, responsive surface coatings, etc.

*Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockhead Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.